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Heat sensitive adhesive composition and heat sensitive adhesive sheet

The presented invention is concerned with a heat sensitive adhesive composition in the form of an aqueous dispersion that is comprised of a thermoplastic resin and a solid plasticizer, with which the thermoplastic resin possesses an average particle dimension of 0.3  $\mu$ m or less, as well as a gel content of 3 to 80%, and also a heat sensitive adhesive sheet that is produced by means of the application of said composition onto a carrier and the drying of this herewith.

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## Description

The presented invention is concerned with a heat sensitive adhesive composition that is not sticky at room temperature, but that will get sticky once it will be heated up.. The invention is also concerned with a heat sensitive adhesive sheet that encompasses a carrier and a heat sensitive adhesion composition that is applied to one of the surfaces of the carrier material, and with which said sheet will be utilized for label or similar purposes.

It is common that labels are applied to glass bottles for non-alcoholic and alcoholic drinks, medications, or chemicals, or similar substances by means of a process, with which said labels will be coated with a water soluble adhesive, such as, casein, starch, or similar materials, and with which said labels will be applied to said bottles with the support of automatic labeling equipment, or similar apparatus, or that they will applied by means of a process, with which a common adhesive sheet will be applied under utilization of a automatic labeling equipment or similar apparatus, and with which said label encompasses a surface material, a layer of an adhesive composition, and a release layer that are laminated onto said sheet in the afore mentioned sequence.

However, a label that is coated with a water soluble adhesive has the problem associated with this that said label will wrinkle when the water soluble adhesive is applied to the backside of the carrier material, and that the resulting labels wrinkle or fold after they have been applied to the glass bottle, and that their corners fold up, which leads to a poor labeling and a reduced appearance of such labels.

On the other hand, labels will be utilized that possess the common structure of an adhesive sheet after the release layer was removed from them. It is not very common that the removed release layers will be collected for recycling purposes. In consideration of the fact that the protection of resources and the protection of the environment have received a lot of attention lately, a heat sensitive adhesive sheet that does not require a release liner has received a lot of attention lately.

A heat sensitive adhesive composition always encompasses a thermoplastic resin, solid plasticizers, and similar substances. A heat sensitive adhesive sheet encompasses a carrier, and a heat sensitive adhesive composition that is applied to one of the surfaces of said carrier material. It is mostly common herewith that the heat sensitive sheet, if utilized as a label, will carry a printed image applied to the other surface. The heat sensitive adhesive composition is not sticky at room temperature, but it will be activated and become sticky for the case that it is heated up in the labeling machine that is equipped with a heating means or an oven. The activation temperature ranges commonly between 50 and 150 °C, and at this temperature range, the solid plasticizer in the heat sensitive adhesive composition starts to melt and provides the thermoplastic resin with its stickiness. Because of the fact that the molten plasticizer

crystallizes very slowly, it thus ensures that the adhesive composition remains sticky over a long time duration, the heat sensitive adhesive sheet, or the label that is coated with said adhesive composition can be applied onto a glass bottle or similar container while the adhesive composition still remains sticky.

Even for the case that the heat sensitive adhesive sheet, or the label will be applied to the glass bottles in a continuous manner with the support of a labeling machine that is equipped with a heating means, the thus applied heat sensitive adhesive sheet will not display any of the damages that are caused by the above described processes that encompass the coating of the back surface of the labels with a water soluble adhesive and the application of said labels onto glass bottles. Furthermore, the heat sensitive adhesive sheet will not require the utilization of a release liner of the kind that is utilized with conventional adhesive sheets, and it has advantages concerning the production costs as well as also concerning the protection of resources and the environmental protection aspects.

However, the heat sensitive adhesive sheet is not satisfactory concerning its adhesive characteristics (strength of adhesion, stickiness, kind of adhesion), specifically for those cases, in which it is applied to polyethylene containers, or similar containers that have a low polarity. Herewith, it is possible that the applied heat sensitive adhesive sheet or label can be removed easily from said containers. Furthermore, for the case that the heat sensitive adhesive sheet will be utilized as a label that is applied onto glass bottles, and that has to identify their content in a correct manner (for example, vials in the medical field, chemical bottles, etc.), an outstanding adhesion is especially required herewith, which ensures that said label can be removed from the glass containers only with much difficulty.

It is the scope of the presented invention to provide a heat sensitive adhesive, as well as a heat sensitive adhesive sheet that possesses an outstanding adhesion to containers that are made of polyethylene or similar materials that possess a low polarity, and to glass bottles or similar containers (for example, vials for containing pharmaceuticals, glass bottles that contain chemicals, etc.) that have the requirement that their content has to be identified correctly.

The inventors of the presented application conducted very elaborate research with heat sensitive adhesive compositions, and they discovered that with the utilization of thermoplastic resins that possess a specific median particle size, as well as a specific gel content, a heat sensitive adhesive composition, and a heat sensitive adhesive sheet will be obtained that possess an outstanding adhesion to glass bottles, polyethylene containers with a low polarity, and similar containers.

The presented invention provides thus a heat sensitive adhesive composition that is present in the form of an aqueous dispersion that encompasses a

thermoplastic resin and a solid plasticizer, and with which the thermoplastic resin possesses a median particle dimension of  $0.3\mu$  or less, and a gel content of 3 to 83%.

The heat sensitive adhesive composition that is produced according to the invention is present in the form of an aqueous dispersing that contains a thermoplastic resin as a solid component, as well as a solid plasticizer. For the case that this is desired, it is possible herewith that an adhesion enhancer, a gliding ability enhancer, or a thickening agent or similar can be utilized as optional additives.

The glass transition temperature of the thermoplastic resin preferably ranges around  $30^{\circ}\text{C}$  or above. The average particle dimension of the thermoplastic resin preferably ranges around  $0.2\mu\text{m}$  or less. Specifically preferred herewith is that the thermoplastic resin meets at least one of the three conditions of an average particle size of  $0.17\mu\text{m}$  or less, a gel content of 5 to 60%, and a glass transition temperature of  $40^{\circ}\text{C}$  or higher.

Herewith preferred is that the thermoplastic resin consists of a copolymer, and that at least one component of it would be a member that is selected from the group that consists of styrole, methyl(meth)acrylate, and acrylnitril, and at least one member that is selected from the group that consists of butadiene, isoprene, butylene and one  $\text{C}_4$  to  $\text{C}_{18}$  alkyl ester of the (meth)acrylic acid.

The term "(meth)acrylic acid" that is used in the description and the claims shall identify acrylic acid and/or methacrylic acid. In the same manner it applies that the term "(meth)acrylate" that is used in the description and the claims shall identify acrylate and/or methacrylate.

The presented invention also provides a heat sensitive sheet that will be produced by means of coating one surface of the carrier material with one of the above described heat sensitive adhesive compositions and a subsequent drying of the applied composition. More precisely said, the heat sensitive adhesive sheet that is produced according to the presented invention is comprised of a carrier material, as well as of a dry, non-adhesive layer that is created on top of said carrier material by means of applying the composition on one of the surfaces of said carrier material, followed by the subsequent drying of said moist coating. Herewith, the heat sensitive adhesive composition is present in the form of an aqueous dispersion that is comprised of a thermoplastic resin and a solid plasticizer, with which the thermoplastic resin possesses an average particle dimension of  $0.3\mu\text{m}$  or less and a gel content of 3 to 83%.

#### (1) Thermoplastic Resin

Utilized as a thermoplastic resin for the heat sensitive adhesive composition that is produced following the invention is a thermoplastic copolymer. The copolymer

possesses an average median particle dimension of  $3\text{ }\mu\text{m}$  or less and a gel content of 3 to 83%.

A thermoplastic copolymer with a median particle dimension of  $0.3\text{ }\mu\text{m}$  or less displays outstanding adhesive characteristics. The average particle dimension is preferably  $0.2\text{ }\mu\text{m}$  or less, specifically preferred is a size of  $0.17\text{ }\mu\text{m}$  or less, and above all, a dimension of  $0.12\text{ }\mu\text{m}$  or less. For the case that the copolymer possesses a particle dimension of  $0.12\text{ }\mu\text{m}$  or less, the resulting adhesive composition displays an outstanding adhesion to polyethylene and similar materials that possess a low polarity. For the case that the median particle dimension is larger than  $0.3\text{ }\mu\text{m}$ , the adhesive characteristics will degrade. The smaller the median particle dimension, the better are the adhesive characteristics. However, for the case that the median particle dimension is  $0.05\text{ }\mu\text{m}$  or less, the viscosity of the copolymer emulsion will get too high, and the availability of the processes for the production of the copolymer will be reduced. Because of these facts, it is of advantage that the median particle dimension of said copolymer preferably ranges above  $0.05\text{ }\mu\text{m}$ . Accordingly, the specifically preferred average particle dimension of the thermoplastic resin ranges from  $0.06$  to  $0.12\text{ }\mu\text{m}$ .

The adhesive composition that encompasses a copolymer with a gel content of 3 to 83% displays outstanding adhesive characteristics. For the case in which the average particle dimension of the copolymer exceeds  $0.3\text{ }\mu\text{m}$ , and the gel content is under 20%, the resulting heat sensitive adhesive composition tends to have a lower cohesive force, and the resulting heat sensitive adhesive sheet would require a long time duration (several hours) to obtain a solid adhesion if it would be activated and applied to the surface of articles. The result of this would be that the obtained adhesive sheet would cause problems for the case that it would be applied to a bottle with a small diameter or similar containers, and the applied sheet would lift off easily partially or entirely from the surface of said containers. For the case that the median particle dimension of said copolymer is  $0.3\text{ }\mu\text{m}$  or less, the resulting adhesive composition will have outstanding adhesive characteristics, and thus, the problems of a lifting-off of the corners of the labels away from the bottle will not occur, not even in those cases in which the gel content is less than 20%. However, for the case that the gel content is less than 3%, it will be difficult to avoid the lifting off of the corners, even if the average particle dimension is  $0.3\text{ }\mu\text{m}$  or less. For the case that the gel content exceeds 83%, the adhesive characteristics will get worse, and the problem would very likely arise that the label that would be applied to a bottle of a small diameter would lift away from the container surface. Because of these facts, the preferred gel content is 5 to 60%, and specifically preferred is a content of 5 to 40%.

In order to avoid that the label will lift-off from the surface of a bottle with a small diameter (in the range of about 8 to 20 mm), the thermoplastic resin is required

to fulfill both conditions of an average particle dimension of 0.3  $\mu\text{m}$  or less, and a gel content of 3 to 83%.

Herewith, it is possible to determine the median particle dimension of the thermoplastic resin with the support of a particle dimension determination device, or by means of an observation with the support of an electron microscope. The content of the copolymer can be determined with the support of the following processes. The copolymer emulsion will be cast onto a glass plate that is equipped with a frame, and it will be subsequently air dried at room temperature, in order to produce a film sample that possesses a thickness of 1 mm. A certain amount (about 0.3 g) of the film sample will be inserted for 48 hours and at room temperature into 100 ml of toluol, and the thus obtained mixture will be filtered through a 300 mesh metal sifter. Following the drying process, the weight of the thus obtained residue will be determined. The gel content will be stated by means of weight percentages of the dry residue, based on the film sample. This means, the gel content will be represented by means of the following equation:

$$\text{Gel content: (\% per Weight)} = 100 \times W_1/W_0$$

with which  $W_1$  identifies the dry weight of the residue, and  $W_0$  the weight of the film sample.

For the case that the copolymer that is utilized as being the thermoplastic resin possesses a glass transition temperature of 30  $^{\circ}\text{C}$  or above, the resulting adhesive composition will have an outstanding gliding ability. A preferred glass transition temperature that ensures an outstanding gliding ability is 40  $^{\circ}\text{C}$ , or higher, and a glass transition temperature of 50  $^{\circ}\text{C}$  is specifically preferred. The higher the glass transition temperature, the better the gliding ability. However, for the case that the glass transition temperature exceeds 70  $^{\circ}\text{C}$ , it is possible that the surface of the heat sensitive adhesive sheet that is created by means of coating the surface of the carrier material with a heat sensitive adhesive composition, has a reduced stability under some circumstances, and for these cases it is difficult to create a printed image on the coated surface. For the case that it is required to create a printed image on the surface that is coated with the heat sensitive adhesive composition, it is specifically preferred that the glass transition temperature of the copolymer ranges between 30 and 70  $^{\circ}\text{C}$ . On the other hand, for the case that the glass temperature is below 30  $^{\circ}\text{C}$ , it is common that a poor gliding ability will be achieved.

The here used term "gliding ability" refers to the following phenomena. A heat sensitive adhesive sheet is commonly stored or handled in the form of a roll or a stack. In this version, the surface of the sheet that is coated with the heat sensitive adhesive is in direct contact with the carrier material. Because of this, it can happen that the surface that is coated with the heat sensitive adhesive adheres sometimes to said carrier material. This phenomenon is called "blocking". For the case that a heat sensitive adhesive sheet possesses a good

gliding ability, the surface that is coated with the heat sensitive adhesive will not adhere to the carrier material, even not in those cases, in which the sheet is stored in the form of a roll or a stack.

The copolymer that is utilized as a thermoplastic resin can be produced by means of conventional emulsion polymerization processes, as long as the obtained thermoplastic resin possesses an average particle dimension of  $0.3\ \mu\text{m}$  or less, and as long as its gel content is between 3 and 83%. Herewith, it is possible that the emulsion polymerization process can either be, for example, a batch polymerization, a semi batch polymerization, a continuous polymerization, a seed polymerization, or a similar polymerization process. The processes for the addition of the reactants and additives are not very limited, and they can consist of the individual batch addition, portioned addition, or continuous addition. Common emulsion substances, polymerization initiators, chain transfer agents or similar substances that are all well known can be utilized in the common manner with the polymerization.

The emulsion agent includes, for example, an amphoteric, surface active agent, an anionic, surface active agent, a non-ionic, surface active agent, or a similar agent. The amphoteric, surface active agent includes, for example, such agents that possess as the anionic unit a carbonic acid salt, the salt of a sulfuric acid ester, salts of the sulfonic acid, and similar salts, and also such that possess as the cationic unit an amine salt, a quaternary ammonia salt, or similar salts.

Specific examples are laurybetain, stearylbetain, lauryl- $\beta$ -alanine, and similar. The anionic surface active agent includes, for example, sulfates of higher alcohols, alkylbenzolsulfonic acid salts, aliphatic sulfonic acid salts and similar salts. Specific examples herewith are sodium dodecylbenzolsulfonate, sodium laurylsulfate, sodium dodecylidiphenyl etherdisulfonate, and similar substances. The non-ionic, surface active agent includes, for example, alkyl ether, alkyl ester, and alkylaryl ether of the common polyethyl glycol. Specific examples herewith are poly(polymerization degree 1 through 30)oxyethylene- $\text{C}_5$  through  $\text{C}_{30}$ -alkyl ester, poly(polymerization degree 1 through 30)oxyethylene -( $\text{C}_1$  through  $\text{C}_{20}$ -alkyl) aryl ether, and similar substances. These emulsion agents can be utilized alone by themselves, or at least two of them can be utilized in combination with each other. The amount of the emulsion agent can be in the common range, and normally it is at about 0.05 to 5 percent by weight amount per 100 weight amounts of the monomer composition.

The polymerization initiators include, for example, inorganic polymerization initiators, such as potassium sulfate, ammonia sulfate, and sodium sulfate, organic polymerization initiators, such as hydroperoxide (for example, cumylhydroperoxide, diisopropylbenzoylperoxide, p-methanehydroperoxide, etc.), peroxides (for example, benzoylperoxide, laurylperoxide, etc.), azo compositions (for example, azobisisobutyronitril, etc.), and polymerization initiators of the redox type that are obtained by means of combining the above mentioned

polymerization initiators with a reduction agent, such as iron sulfate. These initiators can be utilized individually or as a combination of at least two of those agents. The amount of the initiator is not specifically limited, and it can be used from 0.1 to 5 parts per weight per 100 parts per weight of the monomer compositions.

The chain transfer agent includes, for example, phenolic compositions, such as  $\alpha$ -benzyloacrylamide and similar, aldehyde compositions, such as acroleine, methacroleine, benzaldehyde, and similar, aromatic compositions, such as Toluol, triphenylmethane, pentaphenylmethane, and similar, mercaptane compositions, such as t-dodecylmercaptane, n-octylmercaptane, and similar, xanthogene compositions, such as dimethylxanthogenedisulfide, and similar thiurame compositions, such as tetramethylthiuramedisulfide, and similar, thioglycolic acid(ester) compositions, such as thioglycolic acid, octylthioglycolate, an similar, halogenated hydrocarbon compositions, such as dichlormethane, dibrommethane, carbontetrabromide, 1,1,1-trichlortoluol, and similar, and alcoholic compositions, such as t-crotylalealcohol, and similar. The chain transfer agents can be utilized individually by themselves, or in combinations of at least two of these compositions. The amount of the chain transmitter agent ranges commonly at 0.1 to 20 parts per weight per 100 parts per weight of the monomer compositions.

The monomer compositions that can be utilized with the production of the copolymer include, for example, compositions that contain conjugated double bonds, such as butadiene, isoprene, butylene, and similar, aromatic vinyl compositions, such as styrolee,  $\alpha$ -methyl styrolee, and similar substances, ethylenicly unsaturated carbonic acids, such as methyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexy(meth)acrylate, and similar, vinyl cyanide compositions, such as acryl nitril, methacryl nitril, and similar substances, amido containing vinyl compositions, such as acrylamaide, n-methylolacrylamide, and similar, hydroxyl containing compositions, such as 2-hydroxyethylacrylate, 3-hydroxypropylmethacrylate, silicon containing compositions, such as vinyltriethoxysilane,  $\gamma$ -methacryloxypropyltriethoxysilane, and similar compositions, and bifunctional monomers, such as divinylbenzole, ethyleneglycoldimethacrylate, and similar substances. At least two monomercompositions will be used in combination in order to execute the copolymerization.

It is preferred that the thermoplastic resin that is to be utilized in the presented invention is a copolymer that encompasses: (a) at least a member that is selected from the group that consists of styrolee, methyl(meth)acrylate, and acrylnitril, and (b) at least of one member the is selected of the group that consists of butadiene, isoprene, butylene, and one  $C_4$  through  $C_{18}$ -alkylester of the (meth)acrylic acid.



Herewith, it is possible that the amounts of (a) and (b) can be selected from a wide range. However, it is generally preferred herewith that the copolymer furthermore includes about 60 to 90 percentages by weight of (a) and 40 to 10 percentages by weight of (b).

Because of the fact that the utilization of a styrole containing copolymer leads to outstanding adhesion characteristics, it is specifically preferred that the thermoplastic resin that is to be utilized, needs to be a copolymer that contains styrole according to the presented invention. The amount of styrole in the copolymer preferably ranges at 40 percentages by weight or higher, specifically preferred at 50 percentages by weight or higher, and especially specifically preferred at 60 percentages by weight or higher. For this case, it is preferred that the upper limit of the styrole content in the copolymer is 80 percentages by weight, preferably it is 70 percentages by weight.

A copolymer that contains a large amount of styrole possesses a high glass transition temperature, and its utilization leads to an outstanding gliding ability. A copolymer that contains less than 40 percentages by weight of styrole possesses a low glass transition temperature, and its utilization leads to a poor gliding ability. For the case that a copolymer with less than 40 percentages by weight is utilized, the glass transition temperature of the copolymer will be reduced, but it can be kept at 30 °C or higher by means of utilizing another comonomer, or other comonomers that can provide the resulting copolymer with a high glass transition temperature; those can be, for example, methylmethacrylate, ethylmethacrylate, acrylnitril, vinylchloride, or similar materials.

Preferably used as copolymer are, for example: styrolee-butadiene copolymer, styrolee-(meth)acrylate copolymer, styrolee-butadiene-(meth)acrylate copolymer, and those copolymers that are modified with ethylenicly unsaturated carbonic acids.

By means of an appropriate selection of the monomers and the additives (for example, a good emulgator, an initiator, a chain transition agent, etc.), and also of the polymerization conditions, the desired copolymer with the desired particle dimension, and also the desired gel content will be obtained. The selection of the additives and of the polymerization conditions are depending on the ability of the expert of this technology. For example, for the case that large amounts of water in relation to the monomers will be utilized as a polymerization media or emulgation agent, the resulting copolymer will have a small average particle dimension. The utilization of large amounts of chain transition agents reduces the gel content of the resulting copolymer. By means of a suitable selection of the amounts of the initial monomers, additives, and the polymerization conditions, the desired copolymer with the desired median particle dimension and the desired gel content will be obtained.

The thus obtained thermoplastic resin that will be utilized for the production of the heat sensitive adhesive composition according to the invention, and that is contained in said composition, is commonly available in the form of an emulsion that possesses an amount of solid substances of 20 to 80 percentages by weight, preferably of 40 – 60 percentages by weight.

## (2) Solid Plasticizers

The solid plasticizers that can be utilized together with the copolymer that is utilized as being the thermoplastic resin, consist of esters of the benzoic acid, caprylic acid, citric acid, phthalic acid, phosphoric acid and sulfonamide derivations that are commonly identified as being plasticizers, and that preferably possess a melting point of 60 to 80 °C. Preferred examples of such solid plasticizers include: dihenylphthalate, dihexylphthalate (melting point 65 °C), dicyclohexylphthalate (melting point 63 to 65 °C), dihydroabietylphthalate (melting point 65 °C), dimethylisophthalate (melting point 66 to 67 °C), diisohexylphthalate, sucrosebenzoate, ethylglycoldibenzoate (melting point 70 °C), trimethyloethanetribenzoate (melting point 73 °C), glycerinetribenzoate, pentarythritetetrabenzoate (melting point 95 °C), sucroseoctaacetate (melting point 89 °C), tricyclohexylcitrate (melting point 57 °C), n-cyclohexyl-p-toluosulfonamide (melting point 86 °C), and similar substances. For the case that the plasticizer, which is present has a melting temperature that is less than 50 °C, a lower gliding ability will result, while plasticizers that possess a melting point that lays above 100 °C can be difficult to activate by means of heating up.

The solid plasticizer melts for the purpose of its activation for the case that it is heated to a temperature that is not laying below its melting temperature, and it thus softens the thermoplastic resin, and resulting from this is a sticky adhesive mass that acts as a heat sensitive adhesive composition. The time duration over which the composition remains sticky, varies in dependence on the kind of the utilized solid plasticizer. In order to maintain the stickiness over a long time duration, it is preferred to utilize dicyclohexylphthalate herewith.

It is preferred that the solid plasticizer possesses a median particle dimension of 2 to 10  $\mu\text{m}$ , specifically of 3 to 7  $\mu\text{m}$ . For the case that the median particle dimension is less than 2  $\mu\text{m}$ , it is common that a lesser gliding ability will be achieved. However, on the other side, if the median particle dimension is larger than 10  $\mu\text{m}$ , it is unrealistic to believe that the resulting heat sensitive adhesive composition will become sticky fast enough, if it is applied onto a carrier material that is to result in a label. This is because of the fact that it takes a long time until such a plasticizer is molten. The average particle dimension of the solid plasticizer can be determined with the support of a particle dimension measurement equipment, or by means of observation with the electron microscope.

For the purpose of adjusting the average particle dimension of the solid plasticizer onto the above mentioned range, said solid plasticizer will be mixed with a dispersion agent and water. It is of advantage herewith to introduce the resulting mixture into a recirculation ball mill, or in a sand mill, or similar equipment and pulverize it there. The dispersion agent that is utilized can include, for example:

water soluble polymers, such as methyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, poly(meth)acrylate (for example, sodium, potassium, or ammonia salts), polystyrenesulfonic acid salts (for example, sodium, potassium, or ammonia salts), gelatin, and similar substances, as well as surface active agents, such as anionic surface active agents, non-ionic surface active agents and similar materials. For example, the anionic surface active agent includes salts of fatty acids (specifically  $C_3$  through  $C_{30}$  fatty acids), salts of alkyl sulfates (specifically  $C_5$  to  $C_{30}$  alkyl salts), salts of alkylbenzyl sulfonic acid (for example,  $(C_5 - C_{30} - \text{alkyl})\text{benzyl sulfonic acids}$ ), salts of alkyl naphthalene sulfonic acid (for example,  $(C_5 - C_{30} - \text{alkyl})\text{naphthalene sulfonic acids}$ ), alkylsulfosuccinate acids (for example,  $(C_5 - C_{30} - \text{alkyl})\text{sulfosuccinate acids}$ ), salts of alkyl diphenylether disulfonates (for example,  $(C_5 - C_{30} - \text{alkyl})\text{diphenylether disulfonates}$ ), salts of alkyl phosphates (for example,  $(C_5 - C_{30} - \text{alkyl})\text{phosphates}$ ), salts of polyoxyethylenealkyl or alkylaryl sulfates (for example, polyoxyethylene  $C_5 - C_{30}$ -alkyl, or  $(C_1 - C_{20} - \text{alkyl})\text{phenyl sulfates}$ ), and similar substances. The non-ionic surface active agents include, for example:

polyoxyethylenealkyl (for example,  $C_5 - C_{30}$ )ether, polyoxyethylenealkylaryl (for example,  $(C_1 - C_{20} - \text{alkyl})\text{phenyl ether}$ ), polymers or copolymers of ethylene oxide, such as polyoxyethylene, or oxyethyleneoxypropylene blockpolymers, sorbitane fatty acids (for example,  $C_5 - C_{30}$ )ester, polyoxyethylene sorbitane fatty acids (for example,  $C_5 - C_{30}$ )ester, polyoxyethylenesorbitane fatty acid (for example,  $C_5 - C_{30}$ )ester, glycerin fatty acid (for example,  $C_5 - C_{30}$ )ester, polyoxyethylene fatty acid (for example,  $C_5 - C_{30}$ )ester, polyoxyethylenealkyl (for example,  $C_5 - C_{30}$ )amines, alkylanol (for example,  $C_5 - C_{30}$ )amides, and similar substances. Each polyoxyethylene unit of the above mentioned dispersion agent commonly possesses a polymerization degree of about 1 to 30. The above mentioned salts are preferably salts of an alkali metal, such as sodium or potassium or ammonia salts.

The relation of the dispersion agent to the solid plasticizer can be suitably selected from a wide range. However, it is basically preferred that the dispersion agent is utilized in an amount of 0.5 to 10 weight parts, specifically 1 to 5 weight parts per 100 weight parts of the solid plasticizer. For the case that the amount of dispersion agent is less than 0.5 weight parts, the solid plasticizer will basically not be dispersed enough, and the finely distributed primary particles tend to agglomerate again. On the other side, the utilization of more than 10 parts per weight of dispersion agent would lead to reduced adhesion characteristics.

### (3) Heat Sensitive Adhesive Composition

The relation of the solid plasticizer to the resin of the heat sensitive adhesive composition that is produced according to the invention is such that 50 to 300 parts per weight, preferably 100 to 250 parts per weight of the solid plasticizer will be utilized per 100 parts per weight of the thermoplastic resin. For the case that the amount of the solid plasticizer is less than 50 parts per weight, the obtained heat sensitive adhesive composition will commonly not become sticky, and it displays poor adhesion characteristics, and also a poor gliding ability. The utilization of more than 300 weight parts of solid plasticizer leads to a heat sensitive adhesive composition that tends to remain sticky only for a short time duration.

For the case that it is desired, it is possible herewith that stickiness causing agents (adhesion enhancers) of an effective amount can be added to the heat sensitive adhesive composition, in order to provide it with even better adhesion characteristics. Examples of stickiness causing agents include the common state of the art of this technology, such as adhesion enhancers that are based on turpentine resins, adhesion enhancers on a phenol resin base, adhesion enhancers that are based on terpene resins, adhesion enhancers on a petroleum resin base, etc. The adhesion enhancers on the turpentine base include, for example, abietinic acid resins, their hydrated versions, maleine acid adducts, and their metal salts, and ester compositions that will be produced from abietinic acid resins, or of their hydrated versions by means of esterifying with alcohols (for example, glycerin, pentaerythrit, ethylene glycol, diethylene glycol, etc.), as well as other turpentine resins. Preferred example of stickiness enhancers on a terpene base are including homopolymers and copolymers of  $\alpha$ -pinene,  $\beta$ -pinene, dipentene, and similar substances, terpenphenol copolymers and hydrated versions of these polymers.

Herewith, it is preferred that an adhesion enhancer is utilized that possesses a softening point of 70 to 100 °C, and that is available in the form of an emulsion. For the case that the softening point is lower than 70 °C, the heat sensitive adhesive composition tends to stick (blocking) to the material; while the resulting heat sensitive label will generally not become sticky once it is heated for the purpose of activation for the case that the adhesion enhancer possesses a softening point that is over 150 °C.

For the case that an adhesion enhancer is utilized, then the preferred relation is 10 to 150 parts per weight, preferably 30 to 100 parts per weight of the adhesion enhancer per 100 parts per weight of the thermoplastic resin. For the case that less than 10 parts per weight of adhesion enhancers are utilized, it is common that only minimal improvements of the adhesion characteristics will be achieved; while with an amount of more than 100 parts per weight the resulting heat sensitive adhesive composition tends to display a reduced gliding ability.

For the case that it is desired to avoid an adherence (blocking), it is possible to add a gliding ability enhancer (such as starch, flower, clay, silicon dioxide, etc.) in the form of a powder, or in the form of an emulsion to the heat sensitive adhesive composition according to the presented invention, or it is also possible to add small polyolefin particles in the form of a dispersion. For the case that such gliding ability enhancers, or small polyolefin particles are utilized, they are preferred in an amount of 10 to 100 parts per weight, preferably 20 to 50 parts per weight per 100 parts per weight of the thermoplastic resin.

For the case that it is desired, it is possible herewith that by means of adjusting the viscosity of the heat sensitive adhesive composition to a certain range, the separation, agglomeration, or uneven distribution of the solid plasticizer in the heat sensitive adhesive composition can be avoided for the case that the composition will be stored over a longer time duration prior to the production of the heat sensitive adhesive sheet and the application of the heat sensitive adhesive composition onto said heat sensitive adhesive sheet. Herewith, it is possible to create heat sensitive adhesive sheets that possess stable characteristics, or the heat sensitive adhesive composition can quickly be applied onto said carrier material. The heat sensitive adhesive composition with a viscosity in a certain specific range is outstandingly suitable for the production of a heat sensitive adhesive sheet because of the fact that the amount of the composition that is to be applied can be controlled easily. It was additionally discovered that it is possible to avoid degrading the adherence that is caused by undesired migration, or undesired penetration of the heat sensitive adhesive composition into the carrier material by means of adjusting the viscosity of said heat sensitive adhesive composition.

According to an execution version of the invention, the viscosity (Brookfield viscosity) of the heat sensitive adhesive composition that is produced according to the invention can be located in a range of 2000 to 30,000 mPA.s, and preferably of 3000 to 15,000 mPA.s, as determined with a Brookfield viscosity meter at 25 °C and 6 UpM. For the case that the heat sensitive adhesive composition has a viscosity in this range, it is possible to achieve the above-mentioned characteristics upon the production of the heat sensitive adhesive sheet by means of coating a carrier material with the heat sensitive adhesive composition at a temperature that lays between the ambient room temperature and a relative high temperature of about 50 °C.

According to another execution version of the invention, the heat sensitive adhesive composition has a viscosity (Brookfield viscosity) of 15,000 to 100,000 mPA.s, and preferably at 15,000 to 50,000 mPA.s, as determined with a Brookfield viscosity meter at 25 °C and 6 UpM, and a viscosity (Brookfield viscosity) of 15,000 or less (preferably of 3,000 to 13,000 mPA.s) as determined with a Brookfield viscosity meter at 50 °C and 6 UpM. For the case that the heat sensitive adhesive composition has a viscosity in this range, it is possible to achieve the above-mentioned characteristics upon the production of the heat

sensitive adhesive sheet by means of coating a carrier material with the heat sensitive adhesive composition at a temperature that lays between the ambient room temperature and a relative high temperature of about 50 °C. For the case that the viscosity is adjusted to this range, the separation, agglomeration, or uneven distribution of the solid plasticizer in the heat sensitive adhesive composition can be avoided extremely well for the case that the composition will be stored.

For the case that the Brookfield viscosity is lower than 3,000 mPA.s at 25 °C and 6 UpM, it is very often difficult to achieve the above-mentioned characteristic, and for the case that the viscosity is lower than 2,000 mPA.s, it is not at all possible to achieve the above-mentioned characteristics. However, for the case that the viscosity exceeds 15,000 mPA.s, it is rather difficult to apply the heat sensitive adhesive composition onto a carrier material at room temperature, and it is very often impossible to evenly and constantly apply the heat sensitive adhesive composition onto a carrier material for that case that it has a viscosity of over 30,000 mPA.s. However, even if the heat sensitive adhesive composition has a viscosity of 15,000 mPA.s or higher at 25 °C and 6 UpM, or if the composition possesses a viscosity in the range of 3,000 to 15,000 mPA.s as determined with a Brookfield viscosity meter at 6 UpM at a temperature that is lower than the melting point of the solid plasticizer, and preferably under a heating condition of 50 °C or less, it is possible to easily apply the composition onto a carrier material at a temperature that is lower than the melting point of the solid plasticizer, or by means of heating it to 50 °C or less. However, for the case that the viscosity will exceed 100,00 mPA.s at 25 °C, difficulties will result during the handling of the heat sensitive adhesive composition.

For the case that the heating up temperature exceeds the melting temperature of the solid plasticizer, the solid plasticizer will start to melt and the heat sensitive adhesive composition becomes sticky, and this is not desirable. On the other hand, it is preferred to heat up the heat sensitive adhesive composition that is produced following the invention to a temperature that is less than the melting point of the solid plasticizer, or to 50 °C or less. Herewith, it is possible to avoid the creation of solids that would be created otherwise for the case that the heat sensitive adhesive composition would be heated for longer time durations. Solid parts of that kind will be created subsequent to drying processes of a part of the heat sensitive adhesive composition during the heating over longer time durations, and they prevent the creation of an even coating of the heat sensitive adhesive composition on the surface of the carrier material.

It is possible to adjust the viscosity with the support of an effective amount of a thickening agent. The thickening agents that can be utilized with the invention are such that are commonly used with the state of the art of this technology, and they include, for example: inorganic pigments, such as beidellit, hectorit, montmorillonit, bentonit, saponit, magnesium carbonate, silicon oxide, mica, aluminum oxide, and similar substances, cellulose derivations, such as

carboxymethyl cellulose, methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, and similar materials, proteins, such as casein, sodium caseinate, ammonia caseinate, and similar substances, polyurethanes, such as polyoxypropylene glycol diisocyanate copolymer, and polyoxypropylene-polyoxyethylene glycol diisocyanate block polymers, polymers based on alginic acid, such as sodium alginate, propyleneglycol alginate, acrylic resins, such as poly(meth)acrylate (for example, poly(meth)acrylic acid or its salts like sodium, potassium, or ammonia salts), poly(C<sub>1</sub> – C<sub>5</sub>)alkyl(meth)acrylate (for example, polymethyl(meth)acrylate, polyhydroxyethyl(meth)acrylate), poly(C<sub>1</sub> – C<sub>5</sub>)alkylpolyoxyethylene acrylate, polymers of the polyvinyl type, such as polyvinyl alcohol, polyvinyl pyrrolidone, methyl vinyl ether maleinic acid anhydride copolymers, polyvinyl benzyl ether, and similar substances, polymers of the polyether type, such as polyethylene glycol ether, polypropylene glycol ether, propylene oxide - ethylene oxide copolymers, or similar substances.

Each of the above mentioned compositions that are supposed to be utilized as a thickening agent can be premixed in advance with a thermoplastic resin emulsion to adjust the viscosity of said thermoplastic resin emulsion. Subsequently, the emulsion will be mixed with the solid plasticizer, and if so required, with other components in order to thus produce the heat sensitive adhesive composition with the desired viscosity. Alternatively, it is herewith possible to add the thickening agent into a heat sensitive adhesive composition to adjust the viscosity of said composition in this manner.

Herewith, it is of advantage to utilize the thickening agent that is normally of solid condition, as this is the case with the above listed inorganic pigments, cellulose derivations, or casein in a dispersed condition, or dissolved in water, or hot water. Such kinds of solid thickening agents can be dispersed or dissolved by means of adding the thickening agent to water, or to hot water and stirring the mixture subsequently. On the other hand, the thickening agents that are present in the form of an emulsion are always added as such into the thermoplastic resin emulsion, or to a heat sensitive adhesive composition that is stirred subsequent to the addition of such emulsions. For the case that the emulsion like thickening agent has a high concentration or high viscosity, and that this condition causes handling difficulties, it is possible herewith that said emulsion could be thinned down with water.

The thickening agent can be added in an amount that is suitable to provide the desired viscosity to the heat sensitive adhesive composition. Some of the above mentioned thickening agents only possess a very limited thickening ability, and they provide the desired viscosity only for those cases in which they are utilized in large amounts. Under some circumstances, some thickening agents can interfere with the adhesion characteristics of the heat sensitive adhesive composition. The adhesive characteristics can specifically be interfered with in those cases, in which the thickening agent is utilized in large quantities. Because of this reason, it is preferred to utilize a thickening agent that displays

an outstanding thickening action, and will not interfere with the adhesive characteristics, and needs to be used in small quantities only.

Examples of such kinds of thickening agents that lead to an outstanding thickening action, and that do not interfere with the adhesive characteristics are, for example, hectorit, carboxymethyl cellulose, methyl cellulose, hydroxymethyl cellulose, polyurethanes, such as polyoxypropylene glycol diisocyanate copolymers, and polyoxypropylene-polyoxyethylene glycol diisocyanate block polymers, acrylic resins, such as poly(meth)acrylate, polyalkyl(meth)acrylate, polyalkylpolyoxyethylene acrylate, methyl vinyl ether maleinic acid anhydride copolymers, propylene oxide - ethylene oxide copolymers, or similar substances that are mentioned in the above. Preferred among these are carboxymethyl cellulose, polyurethanes, acrylic resins, and methyl vinyl ether maleinic acid anhydride copolymers because they provide specifically good thickening characteristics.

Prior to the addition of the thickening agents, the thermoplastic resin emulsion and the heat sensitive adhesive compositions are of an alkalic nature. Many polymers of the polyacrylate type that are among the above mentioned thickening agents lead to a thickening effect once they are added to alkalic solutions. Prior to their addition to the thermoplastic resin emulsion and the heat sensitive adhesive composition the thickening agents possess a low viscosity and can thus be stirred in very easily, and they are thus very advantageous if one considers their handling characteristics. One can therefore make the statement that acrylic resins are very well suited for their use in combination with the thermoplastic emulsion or the heat sensitive adhesive composition that is produced according to the presented invention.

The amount of the thickening agent that is added to the heat sensitive adhesive composition is such an amount that is suitable to result in the desired viscosity of the composition, and it can vary in dependence on the kind of the utilized thickening agent. However, it basically ranges in the amount of 0.05 to 50 parts per weight of the thickening agent (calculated in the form of a solid substance) per 100 parts per weight of the thermoplastic resin. For the case that the amount of thickening agent is less than 0.05 parts per weight, it is for some circumstances not enough to provide the heat sensitive adhesive composition with the desired viscosity. For the case that the amount is more than 50 parts per weight it is possible that the adhesive characteristics of the heat sensitive adhesive composition can be influenced negatively.

The heat sensitive adhesive composition according to the presented invention is preferably available in the form of an aqueous dispersion that contains a thermoplastic resin and a solid plasticizer as its solid components. For the case that this might be desired, it is possible herewith to add the above mentioned adhesion enhancers, gliding ability enhancers, thickening agents, and similar components in their suitable amounts.



In addition to these components, the heat sensitive adhesive composition can furthermore contain small amounts of an emulsifying agent, as well as trace amounts of a polymerization initiator, and of a chain transfer agent that are utilized for the polymerization of a copolymer that is utilized as being the thermoplastic resin. It is also possible herewith that small quantities of a dispersion agent are present that is utilized for dispersing the solid plasticizer.

Herewith, it is preferred that the quantity of the emulsifying agent (that is utilized in the copolymerization) is present in the amounts of 0.05 to 5 parts per weight per 100 parts per weight of the copolymer in the heat sensitive adhesive composition that is produced according to the invention. It is also preferred that the amount of the dispersion agent (that is utilized for the dispersion of the solid plasticizer) will be selected to be present in the amounts of 0.5 to 10 parts per weight, specifically 1 to 5 parts per weight per 100 parts per weight of the solid plasticizer.

Preferably, the heat sensitive adhesive composition in the form of an aqueous dispersion possesses a content of solids of 20 to 80 percentages per weight, specifically of 40 to 60 percentages per weight in relation to the heat sensitive adhesive composition. For the case that the amount of solids is lower than 20 percent by weight, or higher than 80 percent by weight, the tendency exists that the amount of the heat sensitive adhesive composition that is to be applied onto the carrier material with the support of a coating means is rather difficult to control. It is also preferred to select the content of solids in dependence to the kind of the selected coating machine.

The heat sensitive adhesive composition following the invention is basically produced by means of mixing a dispersion of the solid plasticizer, an emulsion of a thermoplastic resin, and, if so required, an adhesion enhancer, a thickening agent or similar substance. These ingredients will be mixed together until the mixture becomes homogenous. Herewith, it is possible to add these components in any desired sequence, as long as they result in a homogenous mixture. The mixing occurs at a temperature that lays below the melting temperature of the solid plasticizer, and it is commonly conducted at room temperature. For example, it is possible to conduct the mixing process as described in the following. As it is mentioned in the above, the solid plasticizer will be pulverized in water and in the presence of a dispersion agent, and the pulverized dispersion will be mixed with an aqueous emulsion of a thermoplastic resin in such a way that the relation of the solid plasticizer to the thermoplastic resin falls in the above mentioned range. Subsequently it is possible, for the case that it is required, to mix in an adhesion enhancer, a thickening agent, a gliding ability enhancer, and other additives. For the case that it is required it is also possible to add water or to vaporize it in order to adjust the content of solids.

The coating amount of the heat sensitive adhesive composition that is to be applied to the carrier material preferably ranges at 5 to 50 g/m<sup>2</sup>, specifically at 10 to 30 g/m<sup>2</sup>, based on the dry weight. For the case that the amount is less than 5 g/m<sup>2</sup>, the heat sensitive adhesive sheet to be utilized as a label does not possesses enough adhesive force. On the other hand however, for the case that the coating amount exceeds 50 g/m<sup>2</sup>, it takes a long time for the heat sensitive adhesive composition until it is activated by means of heating it up, and this is of an economical disadvantage because of the fact that it is not possible herewith to improve the adhesive characteristics by these means.

It is possible to apply the heat sensitive adhesive composition onto a carrier material by means of brushing it on to it, by means of spray coating processes, by silk screening processes, by gravure printing processes, by offset printing processes, by high pressure processes, or by means of a coating means, such as a Meyer Rod Coater, Kiss Roller Coater, direct roller coater, offset roller coater, gravure roller coater, reverse roller coater, rod coater, doctor blade coater, air knife coater, and similar. The applied composition can be dried with the support of a conventional process that is applied in conjunction with the above described application methods.

The heat sensitive adhesive composition needs to be dried at a temperature that is below the melting temperature of the solid plasticizer that is contained in said composition. For the case that the composition will be dried at a temperature that is above the melting point of the plasticizer, said plasticizer will melt during the drying process, and this will cause the heat sensitive adhesive composition to become sticky. Because of this fact the preferred drying temperature is below 50 °C.

It is preferred that the surface of a dry coating of the heat sensitive adhesive composition that covers the heat sensitive adhesive sheet possesses a Bekk smoothness of 60 to 200 seconds, preferably of 70 to 150 seconds, that is determined following JIS P 8119. For the case that the Bekk smoothness is more than 200 seconds, the heat sensitive adhesive sheet possesses generally less gliding ability. On the other hand, for the case that the Bekk smoothness is less than 60 seconds, it is possible that the resulting adhesive sheet that is activated by means of heating it up in some cases does not posses enough adhesive force, and it tends to poorly adhere to the surfaces of glass bottles.

#### (4) Carrier

The material for the carrier that is to be coated with the heat sensitive adhesive composition that is produced according to the invention can consist, for example, of paper, synthetic paper, film, metal foil, non-woven fabric, textile fabric, and similar materials, as well as a laminate of those materials. The carrier can be coated with numerous other coatings that are commonly used with the state of the art of this technology, such as a heat sensitive coating for printing, a

temperature transfer registering coating, a coating that allows for ink jet printing, a pigmented coating, and similar. The surface that is to be coated with the heat sensitive adhesive composition can be equipped with a sealing coating to strengthen the adhesive sheet, or to prevent the penetration of the composition to penetrate into the carrier material and thus to reduce the adhesion force.

For the case that the heat sensitive adhesive sheet will be utilized as a label, the carrier material must allow for printing onto it. Specifically for those cases in which the label is to be utilized for glass bottles that contain a liquid, such as alcohol free and alcoholic drinks, and medicines, or chemicals, it is preferred that the carrier material possesses an outstanding resistance against water and/or solvents.

Herewith, it is possible that the heat sensitive adhesive composition can be dyed with an ink or similar substance, or it can contain little spheres that expand thermally for adjusting the adhesion force.

It is common that the heat sensitive recording sheet is equipped with an imprint, and with the support of labeling equipment; it is continuously applied to bottles, such as glass bottles for beer, medicines, or chemicals, etc. However, it can also be applied to bottles that consist of polyethylene, or similar materials that contain ketchup, ophthalmic solutions (eye drops), or similar substances.

## EXAMPLES

The following examples shall describe the presented invention in more detail; however, they shall not limit it. If not mentioned differently, the term "part(s)" in the examples means "part(s) per weight". Accordingly "%" means "weight percentages" for the case that it is not indicated to be different.

### Example 1

#### Production of a Dispersion of a Solid Plasticizer

An amount of 100 parts of dicyclohexylphthalate (product of OSAKA ORGANIC CHEMICAL INDUSTRY LTD.) were used as solid plasticizer, and 2.4 parts of a non-ionic surface active agent (brand name: Noigen EA-120, a product of the Daiichi Kogyo Seiyaku Co., Ltd.) were used as a dispersion agent, and said substances were mixed homogenous in water with a concentration (content of solids) of 62%. Subsequently, the mixture was pulverized in a roller ball mill to result in dicyclohexylphthalate particles with an average particle dimension of 4  $\mu\text{m}$ .

#### Production of a Copolymer Emulsion

150 parts of water, 0.1 parts of sodium dodecylbenzenesulfate, 0.5 parts of sodium persulfate, 0.8 parts of t-dodecylmercaptane, 0.5 parts of  $\alpha$ -methylstyrene-dimer, 15 parts of butadiene, 67 parts of styrene, 15 parts of methylmethacrylate, and 3 parts of itaconic acid were introduced into an autoclave, and the mixture was made subject to an emulsion polymerization under constant stirring for 9 hours at a temperature of 70 °C. The transfer amount was 97% or higher. The obtained copolymer emulsion was adjusted to a pH of 8 with the support of an aqueous sodium hydroxide solution, and the not converted monomer, as well as other not required substances were removed by means of water vapor distillation in order to obtain a copolymer emulsion for the utilization in the presented invention.

### Analysis of the Copolymer

#### (1) Measurement of the particle dimension

The copolymer was evaluated by means of an electron microscope, and the size of 500 copolymer particles was measured to determine the average particle dimension.

#### (2) Measurement of the gel content

The copolymer emulsion was cast onto a glass plate and air-dried at room temperature to result in a film thickness of about 1 mm. The predetermined amount (about 0.3 g) of the film sample was inserted for a duration of 48 hours at room temperature in 100 ml of toluene, and the resulting mixture was filtered with a 300 mesh metal sifter. The weight of the obtained residue was determined subsequent to the drying process. The gel content was stated as percentage by weight of the dried residue in relation to the film sample. This means, the gel content was determined following the following formula:

$$\text{Gel content (\% per weight)} = 100 \times W_1/W_0$$

with which  $W_1$  identifies the dry weight of the residue, and  $W_0$  the weight of the film sample.

#### (3) Measurement of the glass transition temperature:

The glass transition temperature of the copolymer was determined with the support of a differential scanning calorimeter (product of the Seiko Instruments & Electronics Ltd., SCC-5020) at a heating-up rate of 10 °C/min, and an initial temperature of -100 °C.

### Production of a Heat Sensitive Adhesive Composition

An amount of 200 parts (calculate as a solid substance) of a solid plasticizer dispersion was homogeneously mixed with 100 parts (calculate as a solid substance) of the above obtained thermoplastic resin (copolymer) emulsion to result in a heat sensitive adhesive composition that had a content of solids of 56%.

### Production of a Heat Sensitive Adhesive Sheet

The above obtained heat sensitive adhesive composition was applied with the support of a reverse roller coater in an amount that correlates with 17.8 g/m<sup>2</sup> to one surface of a sheet, consisting of a double side coated, artificial paper that had a weight of 84.9 g/cm<sup>2</sup> (brand name: Kinfujiryomen <73>, product of the NEW OJI PAPER CO., LTD.). Subsequently, it was dried at 40 °C for 3 minutes to result in a heat sensitive adhesive sheet.

#### Examples 2 through 5

14 different kinds of heat sensitive adhesive sheets were produced in the same manner as this is described in Example 1. Different herewith was that the emulsion polymerization during the production of the copolymer emulsion was conducted with the monomers and other components that are listed in the Tables 1 and 2.

#### Example 16

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 1. Different herewith was that a commercially available, carboxyl modified styrole butadiene copolymer (brand name: SN-337, product of the Sumitomo Dow Limited) was utilized as the thermoplastic resin. The median particle dimension, gel content, and glass transition temperature of the copolymer was determined, and the values are listed in Table 2. Herewith, the obtained comonomers and their amounts were not determined, because of the fact that this copolymer is a commercially available product.

#### Example 17

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 1. Different herewith was that with the production of the heat sensitive adhesive composition a turpentine adhesion enhancer (brand name: Super Ester E-710, product of the Arakawa Chemical Industries, Ltd.) was added to the copolymer emulsion in an amount of 50 parts (calculate as a solid substance) per 100 parts of copolymer.

#### Example 18

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 1. Different herewith was that with the production of the heat sensitive adhesive composition, the thermoplastic resin (copolymer) emulsion, as well as the dispersion of the solid plasticizer were mixed and stirred in order to obtain a homogenous mixture, and an acrylic resin (brand name: Primal ASE-60, product of the Rohm & Hass Company) was added as a thickening agent in an amount of 1.2 parts (calculate as a solid substance) per 100 parts of copolymer. This mixture was subsequently stirred until the resulting mixture was homogenous.

The heat sensitive adhesive composition that was produced in this example had a Brookfield viscosity of 8000cps, determined with the support of a Brookfield Viscosimeter at 25 °C and 6 UpM.

#### Example 19

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 1. Different herewith was that with the production of the heat sensitive adhesive composition, the thermoplastic resin (copolymer) emulsion, as well as the dispersion of the solid plasticizer were mixed and stirred in order to obtain a homogenous mixture, and carboxymethyl cellulose was added as a thickening agent in an amount of 0.4 parts per 100 parts of copolymer. This mixture was subsequently stirred until the resulting mixture was homogenous.

The heat sensitive adhesive composition that was produced in this example had a Brookfield viscosity of 10,000cps, determined with the support of a Brookfield Viscosimeter at 25 °C and 6 UpM.

#### Example 20

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 1. Different herewith was that with the production of the heat sensitive adhesive composition, the thermoplastic resin (copolymer) emulsion, as well as the dispersion of the solid plasticizer were mixed and stirred in order to obtain a homogenous mixture, and a polyurethane (brand name: Primal RM-2020, product of the Rohm & Hass Company) was added as a thickening agent in an amount of 0.2 parts (calculate as a solid substance) per 100 parts of copolymer. This mixture was subsequently stirred until the resulting mixture was homogenous.

The heat sensitive adhesive composition that was produced in this example had a Brookfield viscosity of 14,000 mPA.s, determined with the support of a Brookfield Viscosimeter at 25 °C and 6 UpM.

#### Example 21

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 1. Different herewith was that with the production of the heat sensitive adhesive composition, the thermoplastic resin (copolymer) emulsion, as well as the dispersion of the solid plasticizer were mixed and stirred in order to obtain a homogenous mixture, and methyl vinyl ether maleine anhydride copolymer (brand name: Vismul YK-1, product of the Toho Chemical Industry Company, Ltd.), was added as a thickening agent in an amount of 5.1 parts (calculate as a solid substance) per 100 parts of copolymer. This mixture was subsequently stirred until the resulting mixture was homogenous. The heat sensitive adhesive composition that was produced in this example had a

Brookfield viscosity of 16,000 mPA.s, determined with the support of a Brookfield Viscosimeter at 25 °C and 6 UpM.

#### Example 22

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 1. Different herewith was that with the production of the heat sensitive adhesive composition, the thermoplastic resin (copolymer) emulsion, as well as the dispersion of the solid plasticizer were mixed and stirred in order to obtain a homogenous mixture, and a polyurethane (brand name: SN Thickener A-812, product of the San Nopco Limited) was added as a thickening agent in an amount of 1.0 parts (calculate as a solid substance) per 100 parts of copolymer. This mixture was subsequently stirred until the resulting mixture was homogenous.

The heat sensitive adhesive composition that was produced in this example had a Brookfield viscosity of 9,000 mPA.s, determined with the support of a Brookfield Viscosimeter at 25 °C and 6 UpM.

#### Example 23

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 21. Different herewith was that with the production of the heat sensitive adhesive composition, the thermoplastic resin was applied to the carrier material while being heated to 50 °C.

The heat sensitive adhesive composition that was produced in this example had a Brookfield viscosity of 8,000 mPA.s, determined with the support of a Brookfield Viscosimeter at 50 °C and 6 UpM.

#### Example 24

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 22. Different herewith was that with the production of the heat sensitive adhesive composition, the thermoplastic resin was applied to the carrier material while being heated to 50 °C.

The heat sensitive adhesive composition that was produced in this example had a Brookfield viscosity of 8,000 mPA.s, determined with the support of a Brookfield Viscosimeter at 50 °C and 6 UpM.

#### Example 25

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 2. Different herewith was that with the production of the heat sensitive adhesive composition, the thermoplastic resin (copolymer) emulsion, as well as the dispersion of the solid plasticizer were mixed and stirred in order to obtain a homogenous mixture, and an acrylic resin (brand name: Primal ASE-60, product of the Rohm & Hass Company) was added as a

thickening agent in an amount of 1.2 parts (calculate as a solid substance) per 100 parts of copolymer. This mixture was subsequently stirred until the resulting mixture was homogenous.

The heat sensitive adhesive composition that was produced in this example had a Brookfield viscosity of 9,000 mPA.s, determined with the support of a Brookfield Viscosimeter at 25 °C and 6 UpM.

#### Comparison Examples 1 through 4

A heat sensitive adhesive sheet was produced in the same manner as this is described in Example 1. Different herewith was that with the production of the copolymer, the polymerization was conducted with utilizing the monomers and other components that are displayed in Table 2.

#### Evaluation

The following described method was used for testing the above obtained heat sensitive adhesive compositions concerning their short term shelf live stability, as well as concerning their suitability for production processes; and the obtained heat sensitive adhesive sheets were tested concerning their adhesion force and slipperiness in the below described manner. The results are displayed in the Tables 1 and 2 that follow.

##### (1) Short Term Shelf Live Stability

The heat sensitive adhesive composition was allowed to sit for 24 hours at 25 °C after it was filled into a transparent container that possessed a height of 50 cm. The composition was visually evaluated concerning components that were precipitate.

##### (2) Suitability for Production

It was determined, whether the coating amount of the heat sensitive adhesive composition could be controlled easily for the case that the composition was applied to an artificial paper that was coated on both sides.

##### (3) Adhesion Force

For activation purposes, the heat sensitive adhesive sheet was placed in an oven and heated to 120 °C. Within 3 minutes following the activation by means of heating, the sheet was applied to a glass plate or a polyethylene container. The adhesive force was measured two hours later by means of pulling said sheet away from the surfaces with a speed of 0.3 m per minute, and under an angle of 180°. The evaluation took place according to the following criteria.



A: the sheet displayed an outstandingly good adhesive force of not less than 1000 g/25mm, and the carrier was totally destroyed at the time the measurement was conducted.

B: the sheet displayed an adhesive force of not less than 800 g/25mm, however, the adhesive force was less than 1000 g/25mm, and the carrier was only partially destroyed at the time the measurement was conducted.

C: the sheet displayed an adhesive force of not less than 500 g/25mm, however, the adhesive force was less than 800 g/25mm.

D: the sheet displayed an adhesive force of not less than 350 g/25mm, however, the adhesive force was less than 500 g/25mm, and there were no problems with its practical utilization.

E: the sheet displayed an adhesive force of not less than 350 g/25mm, it was easy to remove it by hand.

#### (4) Slipperiness

One allowed the heat sensitive adhesive sheet that was present in the form of a roll to rest for 3 days either at a temperature of 40 °C, or under the conditions of 40 °C and a relative humidity of 90%. Subsequent to this resting period, the sheet was tested for adhesion (blocking).

A: no adhesion

B: it was possible to detect some slight adhesion; however, there were no problems during its practical handling

C: adhesion was present to such a degree that there were still no problems during its practical handling

D: adhesion was present to such a degree that it was impossible to utilize said sheet in practical applications.

#### (5) Total Evaluation

The quality of the sheet was ascertained from the test results of the adhesive force and the slipperiness.

A: outstandingly good

B: very good

C: good

D: satisfactory for the practical utilization

E: unsatisfactory for the practical utilization

The term "polymerization water" in the Tables 1 and 2 identifies the water that was utilized as a polymerization medium during the production of the copolymer. All amounts of monomers, as well as those of the other additives that are displayed in the Tables 1 and 2 are displayed in parts per weight.

Table 1

	Example									
	1	2	3	4	5	6	7	8	9	10
Butadiene	15	15	22	20.5	30.5	27	31			
Styrole	67	67	60	40.5	40.5	45	45		60	62
Methylmethacrylate	15	15	15	25	10	10	6	73	15	15
2-hydroxyethylmethacrylate										
Acrylnitril				10	15	15	15			
N-methylolacrylamide										
2-ethylhexylacrylate								24		20
N-butylacrylate									22	
Fumaric acid			2		2		3		2	
Itaconic acid	3	3		2				2		2
Methacrylic acid					2			1		
Acrylic acid			1	23					1	1

Table 1 (continuation)

	Example									
	1	2	3	4	5	6	7	8	9	10
$\alpha$ -methylstyrole dimmer	0.5	1.0	0.3			0.3			0.3	0.3
t-dodecylmercaptane	0.8	1.0	0.8	0.6	0.7	0.5	0.7	0.5	0.2	0.3
Sodiumdodecyl benzolsulfaonate	0.2	0.3	0.2	0.2	0.3	0.1	0.2	0.2	0.2	0.2
Alkyl benzy/sulfonate type										
Sodiumpersulfate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Potasiumpersulfate										
Polymerization water	150	200	100	150	200	100	120	150	150	150
Average particle dimension $\mu\text{m}$	0.11	0.06	0.18	0.12	0.06	0.25	0.15	0.11	0.10	1.10
Gel content (%)	35	5	42	75	80	70	75	5	35	38
Glass transition temperature ( $^{\circ}\text{C}$ )	60	60	39	41	30	39	31	61	57	48
Adhesive force (glass plate)	A	A	B	B	B	C	B	A	A	A
Adhesive force (polyethylene container)	B	A	C	C	C	D	C	B	B	B
Gliding ability (40 $^{\circ}\text{C}$ )	A	A	A	A	A	A	A	A	A	A
Gliding ability (40 $^{\circ}\text{C}$ , 90% relative humidity)	A	A	B	A	B	B	B	A	A	A
Total adjustment	A	A	C	B	C	D	C	A	A	B

Table 2

	Example							Comparison Example			
	11	12	13	14	15	16	17	1	2	3	4
Butadiene	5	26	28	39			15	50		29	
Styrole	57	68	55	24			67	39	62	42	
Methylmethacrylate	15	3	10	20	17		15	3	15	10	17
2-hydroxyethylmethacrylate				15	5						5
Acrylonitril			3		10			5		15	10
N-methylolacrylamide					3						3
2-ethylhexylacrylate	20								20		
N-butylacrylate					60						60
Fumaric acid	1	2									
Itaconic acid	2		2	1			3	3	1		
Methacrylic acid									2	2	
Acrylic acid		1	2	1	5					2	5

Table 2 (continuation)

	Example										Comparison Example			
	11	12	13	14	15	16	17	1	2	3	4			
$\alpha$ -methylstyrole dimmer														
t-dodecylmercaptane	0.7	0.5 0.9	0.6	0.8				0.5	0.3	0.3				
Sodiumdodecyl benzolsulfonate	0.2	0.2	0.2	0.2				0.2	0.2	0.2				
Alkyl benzylsulfonate type					2.5									1.5
Sodiumpersulfate	0.5	0.5	0.5	0.5				0.5	0.5	0.5				0.2
Potasiumpersulfate					0.2									
Polymerization water	100	100	120	120	170			150	100	150	120	170		
Average particle dimension $\mu\text{m}$	0.19	0.17	0.13	0.16	0.25	0.17	0.11	0.19	0.11	0.16	0.35			
Gel content (%)	38	40	80	80	80	68	35	88	94	90	80			
Glass transition temperature ( $^{\circ}\text{C}$ )	41	27	28	11	4	13	60	-35	61	35	4			
Adhesive force (glass plate)	B	B	B	B	D	B	A	E	E	E	E	E	E	E
Adhesive force (polyethylene container)	C	B	C	C	D	C	A	E	E	E	E	E	E	E
Gliding ability (40 $^{\circ}\text{C}$ )	A	A	A	B	C	B	A	D	A	A	C	C	C	C
Gliding ability (40 $^{\circ}\text{C}$ , 90% relative humidity)	A	C	C	C	C	C	A	D	A	B	C	C	C	C
Total adjustment	B	C	D	D	D	D	A	E	E	E	E	E	E	E

*(Note by the translator: It seems that text is missing in the original. The page prior to the tables, page 13 of the original, ended as translated in the above. In the original, the tables have the page numbers 14 through 17, and this page, the last page of the document, has the page number 18, but it starts with a partial sentence as translated below.)*

.....sensitive adhesive sheet an outstanding adhesive force.  
The addition of a thickening agent did not display any influence on either, the adhesive force, or the slipperiness in any of the examples.

#### Results of the Determination of the Short Term Shelf Life Stability

The heat sensitive adhesive compositions of the examples 1 – 17 did not contain any thickening agents, and they had a viscosity of 1500 to 1700 cps. A slight precipitation of the solid plasticizer was observed, however, no practical problems occurred herewith.

There was no precipitation of the components observed with the heat sensitive adhesive compositions of the examples 18 – 25, and they displayed an outstanding stability during the short term shelf life tests.

It was specifically easy to control the coating amounts of the heat sensitive adhesive compositions of the examples 19 – 25, and this resulted in even coating layers.

For the examples 18 and 25, the time duration that was required for the production of the homogenous compositions by means of stirring after the addition of the thickening agent, was only half as long as the duration that was required for the identical purpose with the other examples.

#### Patent Claims

1. A heat sensitive adhesive composition in the form of an aqueous dispersion the encompasses a thermoplastic resin and a solid plasticizer, with which said thermoplastic resin possesses an average particle dimension of 0.3  $\mu\text{m}$ , or less, and a gel content of 3 to 83%
2. A heat sensitive adhesive composition according to claim 1, with which the thermoplastic resin possesses a glass transition temperature of 30  $^{\circ}\text{C}$  or less.
3. A heat sensitive adhesive composition according to the claim 1, or claim 2, with which the thermoplastic resin possesses an average particle dimension of 0.2  $\mu\text{m}$ , or less.

4. A heat sensitive adhesive composition according to one of the claims 1 through 3, with which the thermoplastic resin fulfills one of the three conditions: median particle dimension of 0.17  $\mu\text{m}$ , or less, gel content of 5 to 60%, glass transition temperature of 40  $^{\circ}\text{C}$  or higher.
5. A heat sensitive adhesive composition according to one of the claims 1 through 4, with which the thermoplastic resin consists of a copolymer that encompasses at least one composition that is selected from the group that consists of styrole, methyl(meth)acrylate, and acrylnitril, and at least one member that is selected from the group that consist of butadiene, isoprene, butylene, and one  $\text{C}_4$  to  $\text{C}_{18}$  alkylester of (meth)acrylic acid.
6. A heat sensitive adhesive composition according to one of the claims 1 through 5 that possesses a Brookfield viscosity of 2,000 to 30,000 mPA.s, determined at 25  $^{\circ}\text{C}$  and 6 UpM.
7. A heat sensitive adhesive composition according to one of the claims 1 through 5 that possesses a Brookfield viscosity of 15,000 to 100,000 mPA.s, determined at 25  $^{\circ}\text{C}$  and 6 UpM, and a Brookfield viscosity of 15,000 mPA.s or less, measured at 6 UpM, and a heating to a temperature that is located below the melting point of the solid plasticizer.
8. A heat sensitive adhesive composition according to one of the claims 1 through 7 that furthermore contains at least one thickening agent that is selected from the group that includes carboxymethyl celluloses, polyurethanes, acrylic resins, and methylvinyl ether-maleinanhydrid copolymers.
9. The utilization of the heat sensitive adhesive composition according to one of the claims 1 through 8 for the coating of a carrier material that consists of a film or a foil made of paper, synthetic paper, metal, or woven and non-woven fabrics, or of laminates of these materials.
10. A heat sensitive adhesive sheet that encompasses a carrier material, and a dry, and not sticky layer of the heat sensitive adhesive composition according to any one of the claims 1 through 8, and with which said layer is applied to at least one side of said carrier material.
11. A process for the production of a heat sensitive adhesive sheet, characterized in such a way that the heat sensitive adhesive composition that is produced according to one of the claims 1 through 8 will be heated up to a temperature that is below the melting point of the solid plasticizer, and that said composition will be applied to at least one side of a carrier material.

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